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ULTRASONIC MIXING OF EPOXY CURING AGENTS

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I. Introduction

Future generation aircraft need higher performance polymer matrices to fully achieve the weight savings possible with composite materials (ref. 1). New resins are being formulated in an effort to understand basic polymer behavior and to develop improved resins (refs. 2, 3 and 4). Some polymer/curing agent combinations that could be useful, cannot be mixed properly using conventional methods because of the high melting temperature of many potential curing agents. As an example, proper mixing of 4,4'-DABP into MY-720 epoxy resin is difficult to accomplish. When 4,4'-DABP is heated to its high melt temperature (242°C) and mixed into the MY-720, the result is uncontrollable, very rapid curing (ref. 5). If solvent is used to lower the melt temperature of 4,4'-DABP, residual solvent evolution during later processing steps causes voids and degradation of properties in the final part. Another curing agent, 3,3'-DABP is a fluffy low density crystalline material that is difficult to blend into the epoxy by classical techniques.

Most of the curing agents for aerospace epoxy resin systems are aromatic amines. It is known that the use of this class of compounds can lead to deleterious reactions with the human body (ref. 6). Their introduction into the body is potentially enhanced when they are melted (by breathing the vapor) or when they are dissolved in solvents (adsorption through the skin) in open containers.

An ultrasonic mixing technique has been developed which may alleviate these problems. In the current study, this technique has been used to mix the 4,4'-DABP/MY-720 and the 3,3'-DABP/MY-720 systems described above. Two other MY-720 systems, with DDS curing agents which can be hot-melt mixed or solvent dissolved, were also investigated using ultrasonic mixing.

2. Experimental

2.1 Processing and Characterization Equipment

The ultrasonic unit used in the mixing was a Dukane*, Model 40A305A generator with a 43A5 transducer and a 113 horn. Maximum power output for the unit is 300 watts. Kapton polyimide film was taped to the end of the horn to form a cup that holds the resin and curing agent during excitation. The ultrasonic equipment used in the mixing is illustrated in Figure 1.

Gel Permeation Chromatography (GPC) testing was performed on a Waters Associates ALC 202/R401 instrument with a SHODEX GPC-A-802S column and tetrahydrofuran as the solvent. Dynamic mechanical analyses (DMA) were performed on a DuPont 1090 thermal analysis instrument, at a heating rate of 5°C per minute, on a sample size of 3.34 mm x 6.37 mm x 12.2 mm. Thermogravimetric analyses (TGA) were run on a Perkin-Elmer TGS-2 system with an AR-2 autobalance and a UU-1 temperature program controller at a heating rate of 10°C/min. A DuPont 990 thermal analyzer was used for the differential scanning calorimetry (DSC) measurements with a heat-up rate of 10°C/min. Flexural strength and moduli of the specimens were determined in accordance with ASTM procedure D 790, using an Instron TTC M1 testing machine. Moisture conditioning took place in a Blue M Model FR-251B-1X humidity chamber at 61°C (140°F) and 85% humidity.

2.2 Preparation of Polymer Samples

The base epoxy resin used in this study was acquired from Ciba-Geigy Corporation as Araldite MY-720**. The major component of this resin is tetraglycidylmethylenedianiline (TGMDA), shown in figure 2. The four curing agents

*Dukane Equipment, St. Charles, Ill.

**Use of trade names or manufacturers does not constitute an official endorsement, either expressed or implied, by the National Aeronautics and Space Administration.

used were the 3,3'- and 4,4'- isomers of diaminodiphenylsulfone (DDS) and the 3,3'- and 4,4'-isomers of diaminobenzophenone (DABP) (Figure 3). The curing agents were hand mixed into the epoxy resin at 30°C prior to ultrasonic blending. The mixing ratios of the samples were 26.3 parts per hundred, by weight, for the isomers of DDS and 22.5 parts per hundred, by weight, for the isomers of DABP. The appearance of the samples prior to ultrasonic treatment was that of an opaque, lumpy, viscous liquid, each colored a darker shade than the natural color of the curing agent. The samples were then placed in a cup with the top of the ultrasonic horn forming the bottom of the cup (Figure 1). The samples were ultrasonically treated until they became amber colored and transparent. Peak temperature reached while mixing 4,4'-DABP with TGMDA was around 150°C after mixing for 10 minutes. The other three curing agents took between one and four minutes exposure to dissolve, reaching peak temperatures of 90 to 100°C for very short times. A hot melt sample was prepared by melting the 4,4'-DDS diamine in a beaker at 176°C and quickly stirring into the resin which was at 35°C. After mixing, the small sample was chilled very rapidly to 20°C.

2.3 Sample Cure

After ultrasonic mixing, the resin samples were poured into aluminum pans 2.25 inches in diameter. All samples were placed in an air-circulating oven and cured according to the cycle illustrated in Figure 4. Because ultrasonic agitation drives out entrapped air, the samples were not degassed before cure.

3. Results and Discussions

3.1 Polymer Preparation

All curing agents were successfully blended into the epoxy resin by the ultrasonic procedure outlined in the experimental section.

Gel permeation chromatograms of the ultrasonically mixed and melt-mixed 4,4'-DDS/MY-720 are compared in Figure 5. Several analyses indicated no significant differences in the compositions of either mixing technique. The chromatograms for both the hot-melt-blended and ultrasonically-blended samples (lower curves) were simple superpositions of the constituents (upper curves). The chromatograms did not have any peaks that would correspond to higher molecular weight polymerization products.

Several mechanisms can be postulated to explain the successful blending of the epoxies and curing agents. The 20 kHz ultrasonic energy interacts with the resin/curing agent through the direct dynamics of cavitation. Presumably the cavitation causes an effective increase in the solubility of the constituents. During the rarifraction part of the wave, a vapor phase "particle" is generated as a result of reduced local pressure. The collapse of that "particle" into the viscoelastic liquid generates intense acoustic shock waves capable of breaking up the solid particles of curing agent, exposing greater surface area to the resin. The effective solubility is probably further enhanced by the interaction of acoustic streaming and molecular shearing and flexing motions caused by the ultrasonic radiation pressure. The streaming and molecular motions produce intense internal mixing of the liquid.

Another possible enhancement of the solubility may result from the temperature increase at the liquid resin-solid curing agent interface, during the positive pressure segment of the wave cycle. As a result of the increased temperature at the interface, the curing agent molecules would come off of the surface of the grains and immediately be advected away from the surface by the streaming currents before too much polymerization occurs.

3.2 Polymer Characterization

All samples were cured according to the schedule shown in Figure 4. This profile is a standard cure for the 4,4'-DDS/MY-720 system. All samples were cured at the same time in the same oven in order to minimize unwanted experimental variables. The cure cycle was thought to be acceptable for 3,3'-DDS and 3,3'-DABP because the functionality and melt temperatures were similar to 4,4'-DDS. However, the cure cycle was questionable for the 4,4'-DABP system because its melt temperature was almost 100°C higher than the other three diamines. This was confirmed when the profile of each cured resin system was studied by DSC (Figure 6). The cure exotherm that occurs between 200-300°C was quite large for the 4,4'-DABP system. The exotherms for the other three systems were small in comparison.

The DMA curves for the four cured polymers are shown in Figure 7. All four systems exhibited similar mechanical energy damping characteristics in the low temperature region, centered around -40°C. In the higher temperature transition region both DDS amines and 3,3'-DABP had apparent glassy transitions around 180°C, with the 4,4'-DABP glassy transition at 120°C. Incomplete cure of the 4,4'-DABP system was verified when the apparent glass transition temperatures (T_g) of the polymers were determined by DMA (Figure 7). The T_g for the 4,4'-DABP was approximately 60°C lower than the other systems. There was an additional transition that was found above the glass transition for the 4,4'-DDS system. This may be indicative of a more complex crosslinked structure for this particular system, i.e., a primary and secondary matrix may have formed during the cure. The damping in the 260°C region may be due to the secondary matrix.

The decomposition temperatures of all systems were quite similar as shown in Table 1 and Figure 8. The comparison of saturated moisture uptake and

apparent glass transition temperature of the cured resins are also shown in Table 1. The incompletely cured 4,4'-DABP system absorbed over 11% water, while the other three systems absorbed about 5% water, by weight.

3.3 Mechanical Testing

Flexural strength averages of the four systems varied from a low of 20.9 ksi for 4,4'-DABP to a high of 25.8 ksi for 3,3'-DABP (Table 2). Strength values and their standard deviations were very good, particularly for the 3,3'-DDS system (refs. 3,7). The highest flex strength value for an MY 720/DDS system in reference 3 was 20.3 ksi and the lowest was 13.3 ksi. Reference 7 reports an average flex strength of 18.2 ksi for an MY 720/4,4'-DDS/SU8 baseline system.

4. Conclusions

Ultrasonic mixing of resins is a useful technique to dissolve solid curing agents into liquid resins to obtain uniform mixing while avoiding uncontrolled advancement of the resin. This technique also precludes the need for solvents that give processing problems during final cure. Under ultrasonic exposure four epoxy resin/curing agent crude mixtures were transformed to homogeneous, transparent, viscous amber liquids.

The 3,3'-and 4,4'-DDS and the 3,3'-DABP curing agents were adequately blended and cured as evidenced by physical and mechanical properties. The higher-melting 4,4'-DABP was successfully blended into the epoxy resin, but both physical and mechanical testing indicated an incomplete cure had occurred for the cure cycle that was used. As a result of this study we have concluded that the ultrasonic blending of solid curing agents into liquid resins such as epoxies is feasible and that cure cycles must be individually developed for each epoxy system.

5. References

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TABLE I. PHYSICAL PROPERTIES OF DIAMINE CURED EPOXIES

AMINE	3,3' DDS	4,4' DDS	3,3' DABP	4,4' DABP
POLYMER DECOMPOSITION TEMPERATURE FOR 10% WEIGHT LOSS (°C)	342	338	331	341
APPARENT GLASS TRANSITION TEMPERATURE (DMA) (°C)	194	181	181	121
SATURATION MOISTURE CONTENT (%)	4.6	5.5	4.5	11.7
APPEARANCE	TRANSPARENT REDDISH-BROWN			

TABLE II. MECHANICAL PROPERTIES OF DIAMINE CURED EPOXIES

AMINE	3,3' DDS	4,4' DDS	3,3' DABP	4,4' DABP
FLEXURE STRENGTH (PSI)	25 800	24 400	24 200	20 900
STANDARD DEVIATION	200	900	1200	2400
FLEXURE MODULUS (PSI)	610 000	580 000	630 000	640 000

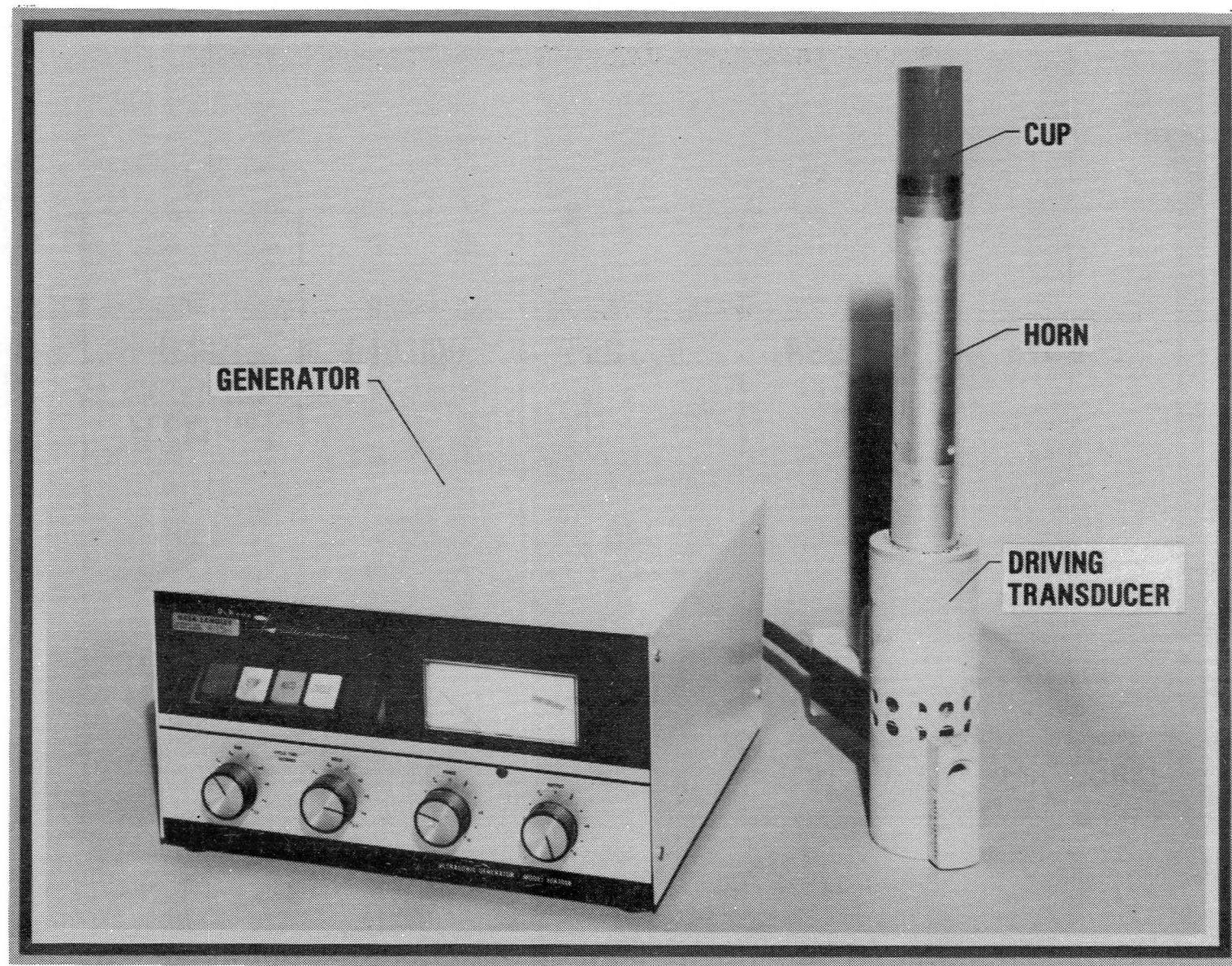
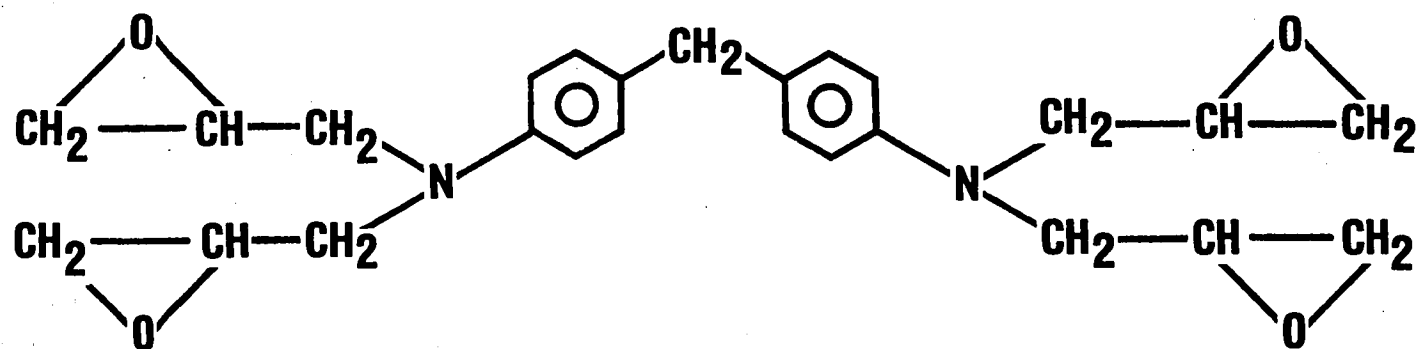


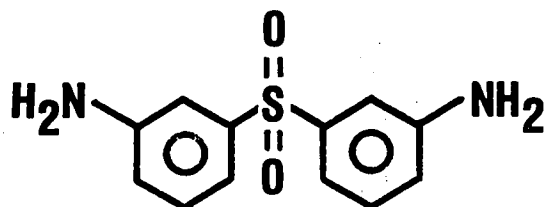
FIGURE 1. ULTRASONIC MIXING EQUIPMENT



APPEARANCE: VISCOUS AMBER LIQUID

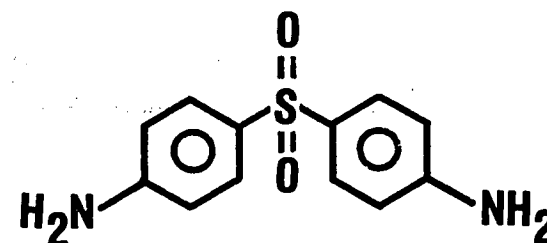
FIGURE 2. EPOXY MONOMER: TETRAGLYCIDYLMETHYLENEDIANILINE

3,3' DDS



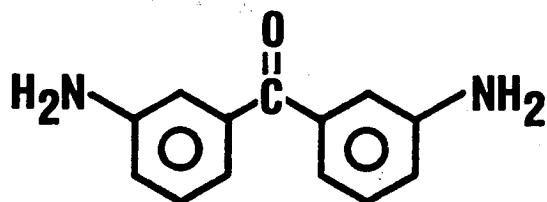
MELT TEMPERATURE, 168°C
APPEARANCE; FINE FLOCCULENT POWDER
RELATIVE DENSITY; LOW

4,4' DDS



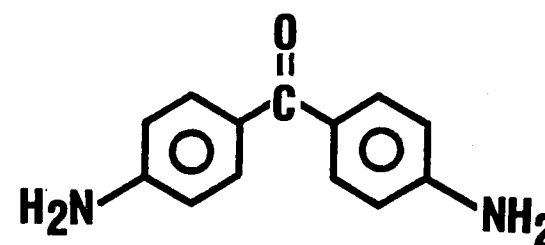
MELT TEMPERATURE, 175°C
APPEARANCE; FREE FLOWING POWDER
RELATIVE DENSITY; MEDIUM

3,3' DABP



MELT TEMPERATURE, 149°C
APPEARANCE; CRYSTALLINE NEEDLES
RELATIVE DENSITY; LOW

4,4' DABP



MELT TEMPERATURE, 242°C
APPEARANCE; LARGE, GRANULAR
RELATIVE DENSITY; HIGH

FIGURE 3. DIAMINE CURING AGENTS

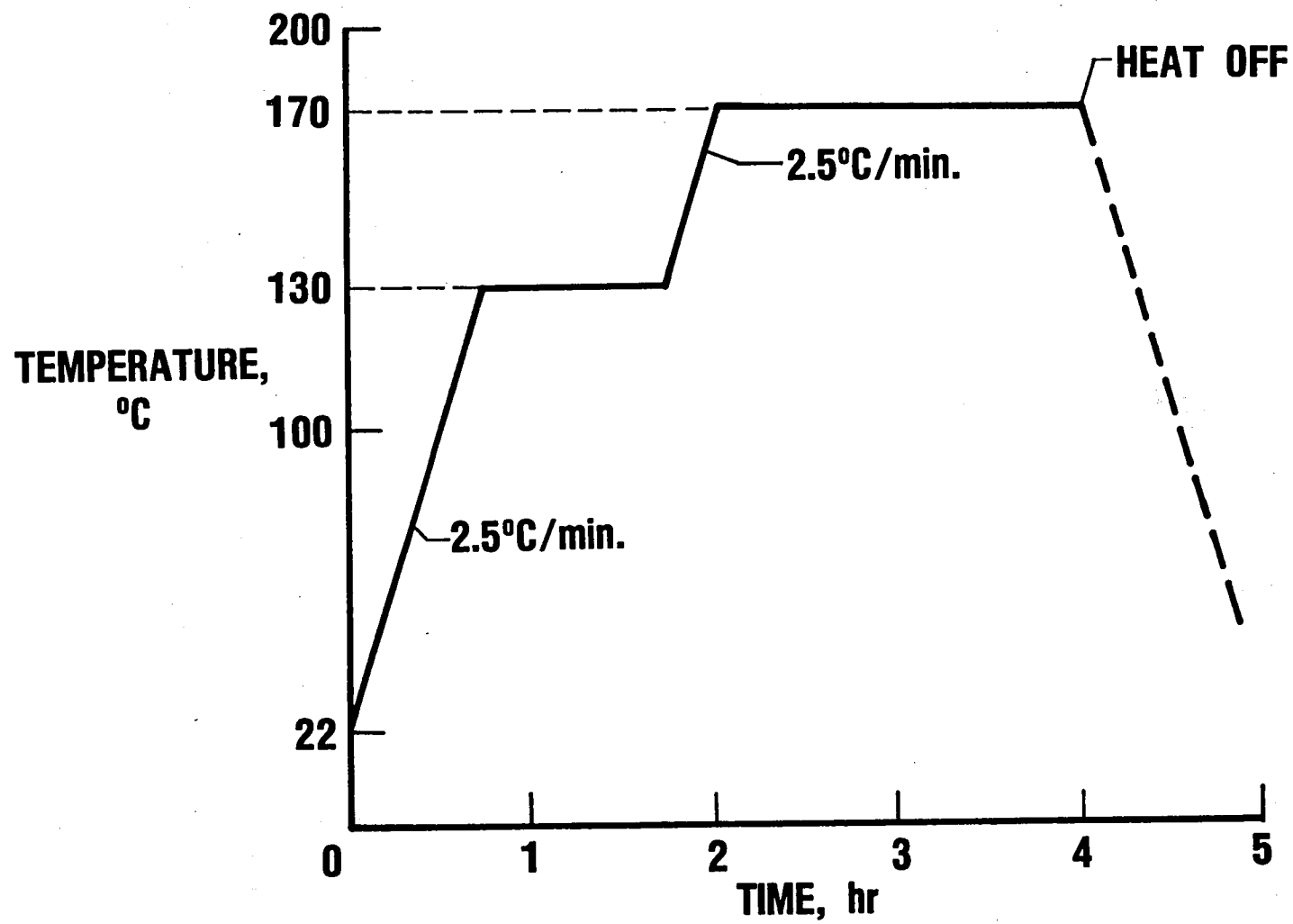


FIGURE 4. OVEN CURE CYCLE FOR DIAMINE CURED EPOXIES

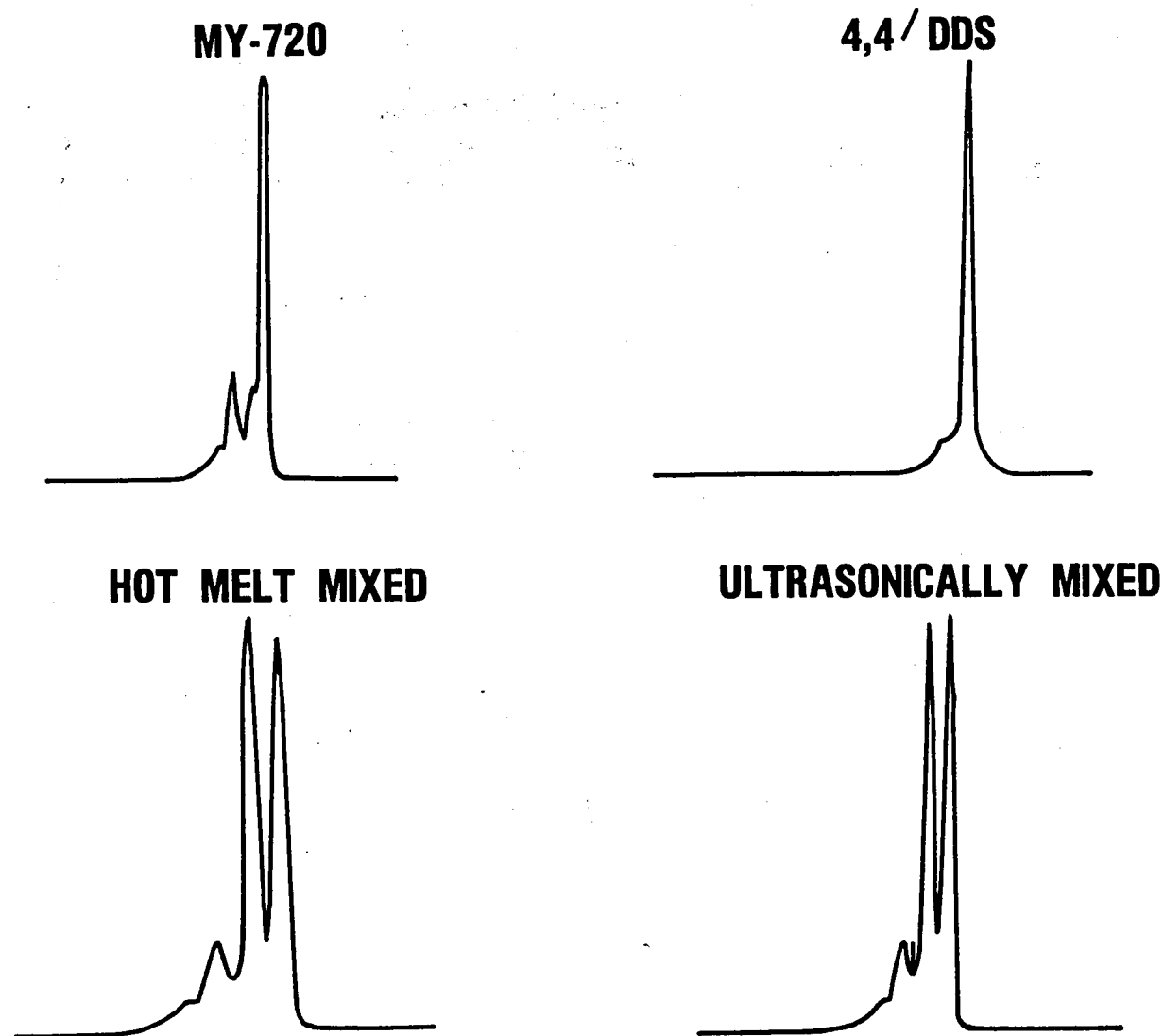


FIGURE 5. GEL PERMIATATION CHROMATOGRAMS OF HOT MELT AND ULTRASONCIALLY MIXED EPOXY RESINS

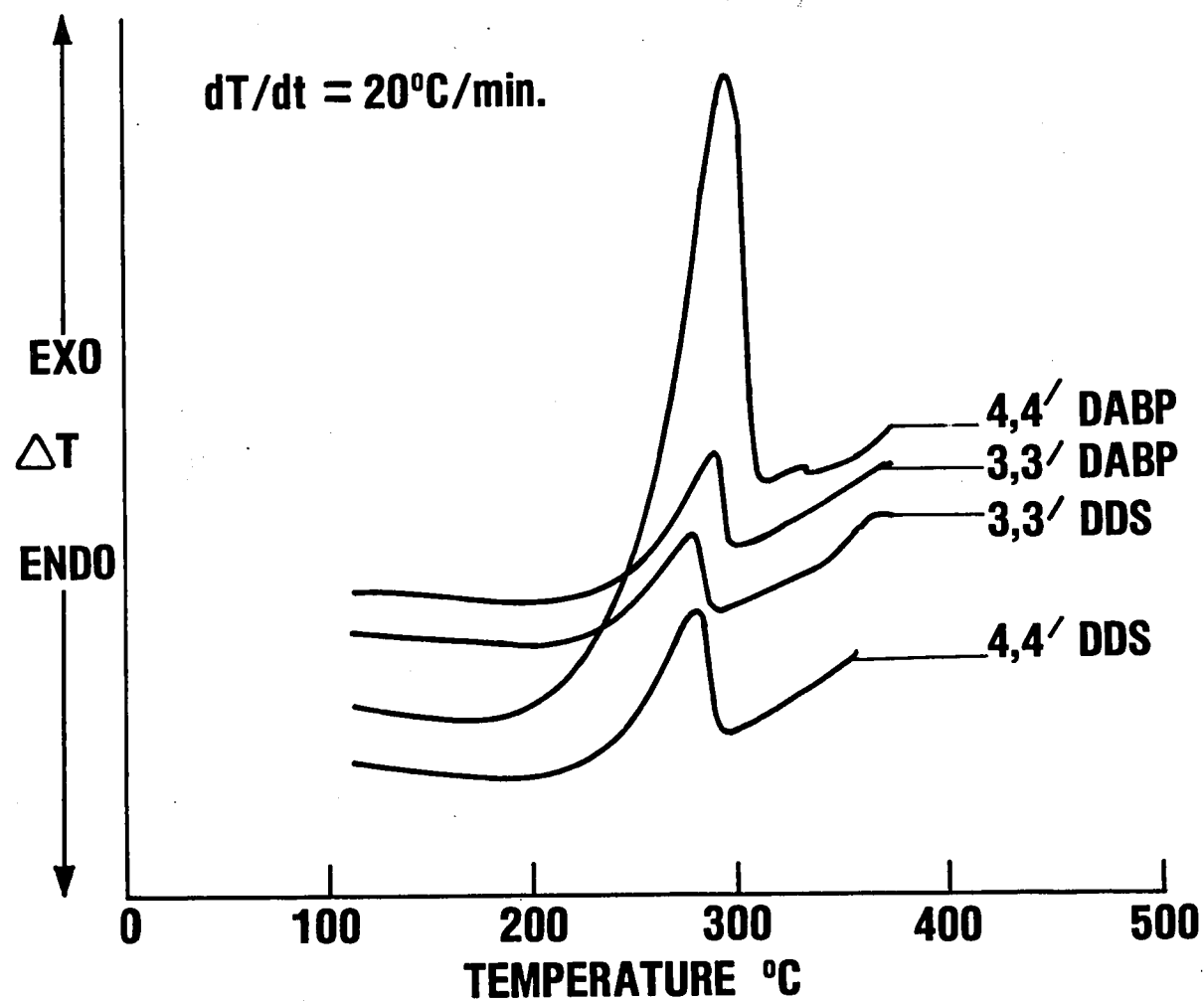


FIGURE 6. DIFFERENTIAL SCANNING CALORIMETRY OF DIAMINE CURED EPOXIES

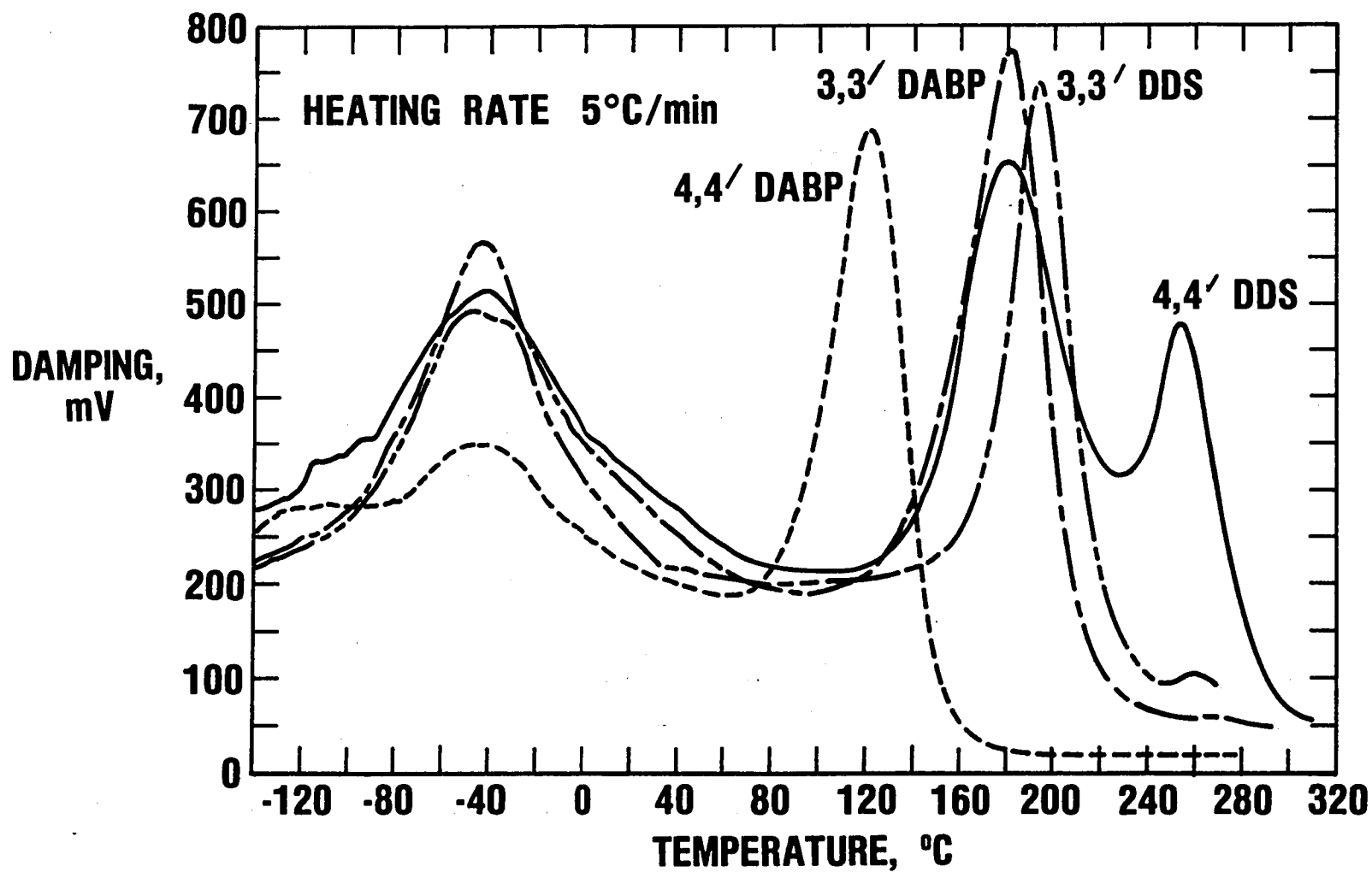


FIGURE 7. DYNAMIC MECHANICAL ANALYSES OF DIAMINE CURED EPOXIES

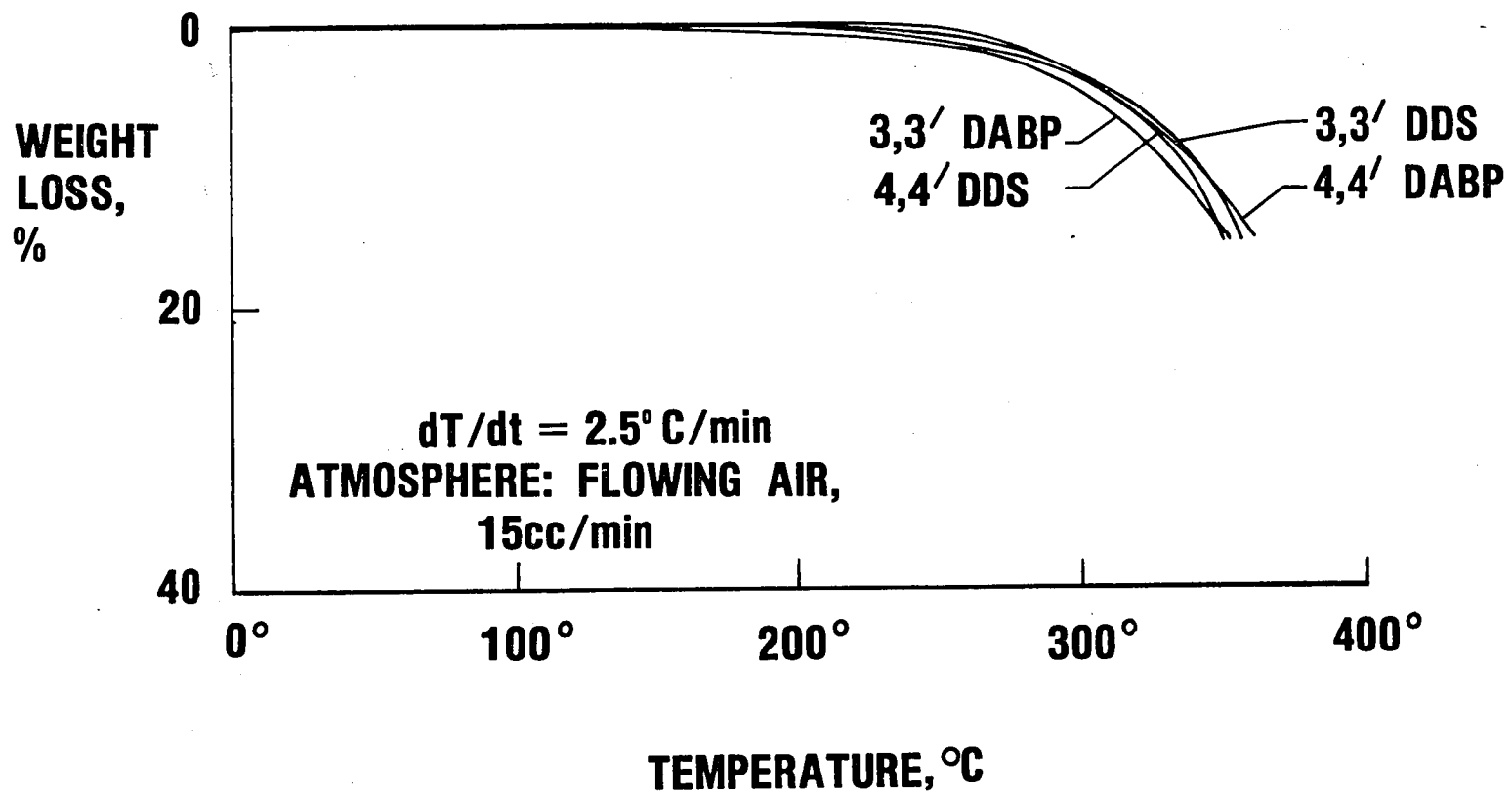


FIGURE 8. THERMOGRAVIMETRIC ANALYSES OF DIAMINE CURED EPOXIES

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16. Abstract A new technique for mixing solid curing agents into liquid epoxy resins using ultrasonic energy has been developed. This procedure allows standard curing agents such as 4,4'-diaminodiphenyl sulfone (4,4'-DDS) and its 3,3'-isomer, (3,3'-DDS) to be mixed without prior melting of the curing agent. It also allows curing agents with very high melt temperatures such as 4,4'-diaminobenzophenone (4,4'-DABP) (242°C) to be mixed without premature curing. Four aromatic diamines were ultrasonically blended into MY-720 epoxy resin. These were 4,4'-DDS; 3,3'-DDS; 4,4'-DABP and 3,3'-DABP. Unfilled moldings were cast and cured for each system and their physical and mechanical properties compared.					
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